ENVIRONMENTAL PROTECTION

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USE OF INDUSTRIAL WASTES IN PRODUCTION OF CERAMIC PIGMENTS

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Ceramic pigments, which are microgranules of wastes formed in polishing optical glass whose surface is coated with two layers — silica and crystals of α-Fe_2O_3, α-Al_2O_3, and $FeAl_2O_4$, were synthesized. The pigments obtained can be used for preparation of enamels for glass, metal, and porcelain.

Manufacturing pigments made from industrial wastes would not only solve the important environmental problem of utilizing them but would also expand the raw-material base for production of ceramic pigments by widely using local material resources for this purpose.

A trend toward manufacturing materials for different applications by attaching nanoparticles on the surface of microgranules of metals, oxides, sulfides, carbon, etc., has recently been noted [1]. The nanoparticles attached on the surface lose the ability to adhere, have high reactivity in reacting with binders, have chemical resistance to acid and basic media, and have good thermal stability. The development of materials with localized microparticles on their surface is a pressing problem.

We investigated the possibility of obtaining ceramic pigments from wastes from polishing optical glass (OGW) by forming a coating of metal oxide particles on the surface of the base microgranules.

OGW slip, which is a pasty aqueous mixture of finely disperse optical glass powders and abrasive powder — electrocorundum, glycerin, soda emulsion, SF — was used for the study. The slip was dried at 100 ± 5°C to the powdered state, and the powder obtained was screened through a sieve with 40 μm mesh diameter.

The surface of the OGW particles was coated with a silica gel film with high activity with respect to an important number of chemical compounds with different functional groups [2]. The method in [3] was used for this. A weighed portion of OGW powder was mixed in a LR-10 electric stirrer (600 min^{-1} rotation rate) in hot distilled water (98°C). A solution of liquid soda glass (LSG) of the composition $Na_2O \cdot 2.45SiO_2$ (GOST 13079–81) was added by drops to the suspension obtained. The mass content of SiO_2 in the LSG solution was 2%, and the ratio of OGW powder to SiO_2 was 7 – 8 (bath ratio). The volume of the initial suspension was kept constant during addition of the LSG solution. In boiling aqueous solutions of LSG, sodium silicate is hydrolyzed, and caustic soda and silica gel SiO_2 are formed as a result [4].

After addition of the entire calculated amount of LSG solution, heating was continued for 1 h, then the suspension was cooled to room temperature, and the sediment obtained was washed on a filter with distilled water. After the sediment was dried at 100 ± 5°C, it was treated with heat at 500°C in a muffle furnace for 3 h.

Single-stage precipitation of metal hydroxides from 0.5 – 1.0 M $FeSO_4$ solution and 0.5 – 2.0 M $Al_2(SO_4)_3$ solution was conducted on the surface of OGW particles modified with the LSG solution at 85°C (pH = 7 – 8) while intensively stirring for 1 h. The sediment obtained was washed by decantation with hot distilled water to a negative reaction for SO_4^{2-} ion in the washing waters and filtered off. Washing was monitored with 2% $BaCl_2$ solution. The samples dried at 100°C were heated at 800°C for 3 h.

The method of determining the zeta potentials was used to monitor formation of a bilayer coating on the surface of the OGW. The following parameters of experimental 0.05% aqueous solutions were measured on a Zetaphorometer IV microelectrophorometer (France): viscosity, dielectric constant, electrophoretic mobility of particles. The value of the ζ potential was calculated with the Smoluchowski equation:

$$\zeta = \frac{4\pi\mu\eta}{\varepsilon},$$

where μ is the electrophoretic mobility of the particles; η is the viscosity; ε is the dielectric constant.

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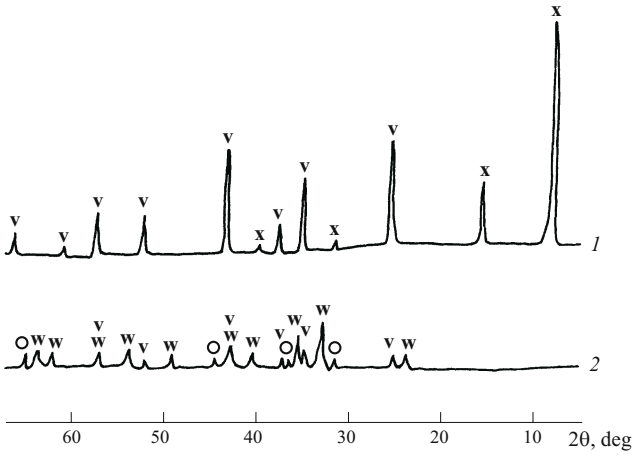

Fig. 1. X-ray patterns of samples: *1*) OGW; *2*) pigment; **v**) α-Al_2O_3; **x**) β'-$NaAl_7O_4$; **w**) α-Fe_2O_3; ○) $FeAl_2O_4$.

The x-ray patterns of the samples were taken on a DRON-3 diffractometer (CuK_α radiation, Ni filter). Differential thermal analysis was conducted in corundum crucibles with a MOM derivatograph with a temperature elevation rate of 10 K/min and a 500 mg sample. Cp calcined aluminum oxide was used as the standard.

The structure of the surface of the experimental powders was investigated in a LEO 1420 scanning electron microscope at magnification of 2000, 5000, and 10,000 times. A gold layer was sputtered on the surface of the samples in a VUP-2K vacuum sputtering instrument.

It was found that after treatment of previously positively charged OGW particles (ζ potential equal to 7.63 mV) with the negatively charged LSG solution (ζ potential of – 7.81 mV), their surface acquired a negative charge (ζ potential equal to – 5.28 mV). This suggests that the silica gel, SiO_2, coagulates directly on the surface of the OGW particles. After precipitation of metal hydroxides on the negatively charged surface of the silica-gel film from aqueous solutions of the indicated salts (ζ potential equal to 3.35 mV), the charge of the particles in the coagulant obtained again became positive (ζ potential equal to 2.01 mV). Recharging of the surface of the particles was thus observed in each stage of treating the coating. As a consequence, coagulation of SiO_2 gel and precipitation of hydroxides take place directly on the surface of the OGW particles.

The data from x-ray phase analysis indicate that the initial OGW powder contains corundum α-Al_2O_3 and sodium aluminate β'-$NaAl_7O_{11}$, probably formed as a result of the reaction of the components of the optical glasses with the electrocorundum in the conditions of basic medium and high temperature, which increase in rubbing the surfaces in polishing (Fig. 1, curve *1*). The glass contained in OGW is x-ray amorphous. Two endothermic effects with maxima at 135 and 620°C and an exothermic effect at 320°C are observed in DTA of the initial OGW powder. The first endothermic effect, related to a change in the weight of the sample, corresponds to liberation of adsorbed water vapors and the second corresponds to melting of the sample (Fig. 2*a*). Total decomposition of glycerin and SF takes place in the 260 – 410°C temperature range. The total amount of weight loss at 410°C is 2%.

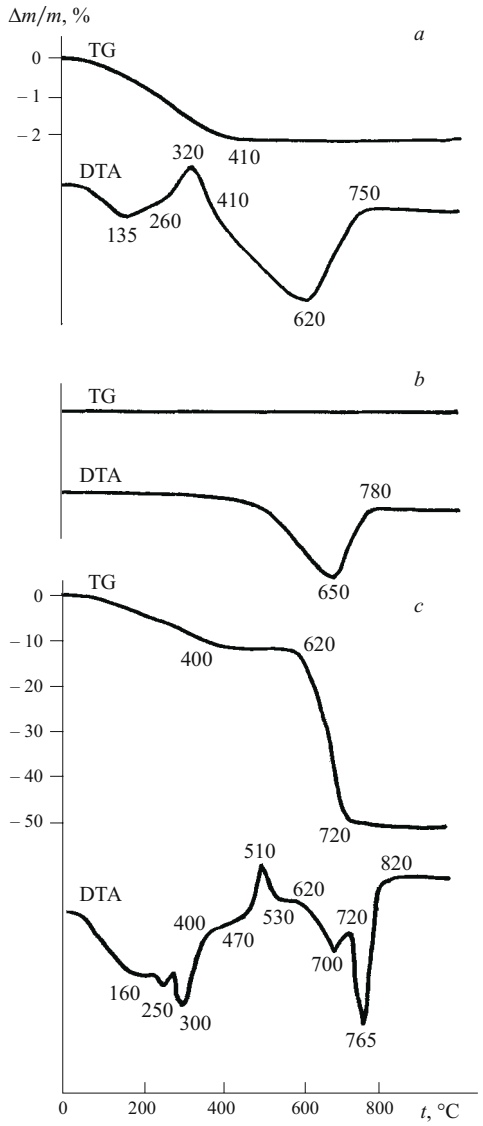

Fig. 2. Results of complex thermal analysis of samples: *a*) OGW; *b*) OGW with silica-gel coating; *c*) pigment.

The derivatogram of OGW powder modified with LSG solution has one pronounced endothermic effect with a maximum at 650°C not related to a change in the sample weight and due to melting of the sample (Fig. 2*b*). It should be noted that OGW powder whose particles are coated with a silica layer has high refractoriness, and the melting point of the sample increases by 30°C. The x-ray phase analysis of this powder did not show the presence of any new phases, since the silica formed is x-ray amorphous.

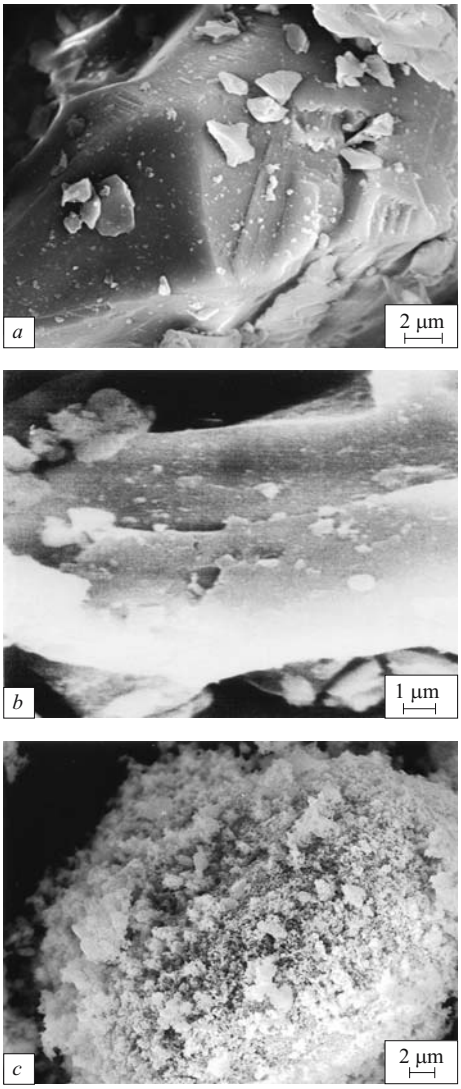

Fig. 3. Electron-microscopic photographs of samples: *a*) OGW; *b*) OGW with silica gel coating; *c*) pigment.

The initial OGW powder consisted of irregularly shaped particles (from 1 to 20 μm) with pronounced surface relief (Fig. 3*a*). The OGW microgranules modified with the LSG solution are coated with a nonporous silica film which hides the initial texture of the particles (Fig. 3*b*). The initial shape of the OGW particles persists after application of the silica layer.

In the electron-microscopic photographs of the pigments, note that the surface of the particles of the synthesized pigment are totally coated with a crust of flaky crystals (Fig. 3*c*). The initial particle shape is not preserved.

Four endothermic effects with maxima at 250, 300, 700, and 765°C are observed in the derivatogram of the pigment powder made from OGW powder with a silica coating and dried at 50°C. The first three are accompanied by a decrease in the weight of the sample (Fig. 2*c*). The data on the weight change during heating show that the sample loses 10% of the weight in the first stage (up to 400°C), the weight of the sample is almost unchanged in the second stage (400 – 620°C), and the sample loses 40% of its weight in the third stage (620 – 720°C). The total amount of weight loss at 720°C is 50%. The endothermic effect at 765°C not related to any weight change is due to melting of the sample. In the 470 – 530°C temperature range, there is an exothermic effect at 510°C not related to any change in the sample weight and probably caused by the formation of spinel and possible crystallization, which is in agreement with the data from XPA and the results in [5]. In XPA of the pigment made from OGW with a silica layer, $FeAl_2O_4$, α-Fe_2O_3, and α-Al_2O_3 spinel was identified (see Fig. 1, curve *2*).

The synthesized pigments are light to dark brown in color as a function of the composition. The effect of the firing temperature on the color characteristics of the pigments in the coatings was investigated to determine whether they could be used to obtain colored enamels and glazes.

The pigments were mixed with lead-free enamels (TU RB 100029049.030), industrial cover ÉPS-117, and LG-19 glaze. The mass content of the pigments in the compositions was 3 – 10%. The compositions were applied on glass, primed metal, and porcelain supports with generally accepted technology. The decorated glass samples were fired at 580 – 590°C, the enameled metal samples were fired at 850 – 900°C, and the porcelain was fired at 1000°C. The fired coatings were characterized by good luster and absence of crazing. The color of the pigments did not change after firing, which demonstrates their stability in a glass melt in high-temperature conditions.

These studies thus demonstrated the possibility of using thermostable pigments made from industrial OGW by forming an intermediate silica gel film on the surface of their microgranules followed by formation of a strongly retained surface layer consisting of α-Fe_2O_3, α-Al_2O_3, and $FeAl_2O_4$ crystals on it. The pigments obtained can be used for preparing cover enamels of metal and for decorating glass and porcelain ware.

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